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Angle resolved XPS of monomolecular layer of 5-chlorobenzotriazole on oxidized metallic surface

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ABSTRACT

Angle resolved XPS is used to study adsorption of 5-chlorobenzotriazole (5-chloroBTAH) on surfaces of the oxidized metals: mild steel, copper and zinc from borate buffer solution (pH 7.4). It is shown that for the metals studied the 5-chloroBTA anions, when adsorbed, form a monomolecular layer whose thickness is ~6 Å comparable with the size of BTA. As XPS evidences adsorption proceeds with deprotonation of 5-chloroBTAH and formation of the coordination bonds between the lone pair of nitrogens and cation of a metal. Measuring XPS at two different angles unequivocally points out almost vertical arrangement of the anions toward the sample surface, when chlorine atoms form outmost virtual layer.

1. Introduction

Interaction between a surface of a metal and the first layer of organic molecules plays defining role in properties of a surface. This interaction determines a structure and properties of such modified surface, which in turn influences the formations of the further layers. The first layer adsorption can have both chemical and the physical nature. In case of the former, chemisorption occurs due to the chemical bonding between a metal cation and an organic molecule, in the second one the adsorption is based on interaction owing to dispersion forces [1,2].

Adsorption can come to the end either by formation of the single monomolecular layer or multiple layer formation. In the first case, it can form a nanosize self-assembled monomolecular layer [3,4], which can give new functional properties to the surface that finds an application in various processes, including in developing new anticorrosive coatings. At last, on such modified surface the second and subsequent layers can be formed that in turn may naturally improve adsorbate protective capacity.

Thereupon a study revealing a composition and a structure of surface monomolecular layers is of a great interest. A method of scanning tunnel microscopy is quite valuable in establishing a spatial arrangement of molecules on a surface of metals, which, however, demands using single-crystal samples [4]. Often for studying adsorption of organic molecules, the method X-ray photoelectron spectroscopy (XPS) is used [5], which allows assessing the qualitative and quantitative composition of a surface, and thickness of the layers formed on a surface. Measuring angle resolved XPS together with the presence of several heteroatoms in adsorbate helps in many cases to reveal orientation of molecules relative to a surface [6].

Among a large variety of organic molecules used as corrosion inhibitors, a class of azoles is especially valuable, in particular 1,2,3-benzotriazole $C_6H_4N_3H$ (BTAH and BTA are molecular and anionic forms, respectively), which is considered in many publications [see reviews 7-10]. BTAH and its derivatives are used as efficient corrosion inhibitors for metals and alloys in various environments. Nevertheless, the questions related to formation of the primary layer, the nature of interaction, orientation of molecules still remain unclear [10].

Fe, Cu, Zn and their alloys are the most used in industry, often in combination, and require application of corrosion inhibitors. Because three metals have quite different electrochemical properties, it is of interest to find some regularities and differences in the formation of the adsorbed monomolecular films. Therefore in the present work the angle resolved XPS is used to study a monomolecular layer of 5-chloroBTA (derivative of BTAH) (Fig. 1) formed on the oxidized metals: mild steel, copper, and zinc. From XPS analysis we have obtained information on “in-depth” distribution of the adsorbed overlayer and a spatial arrangement of 5-chloroBTA.

On the other hand, using three different metals give an opportunity to estimate the capability of Multiquant software to calculate

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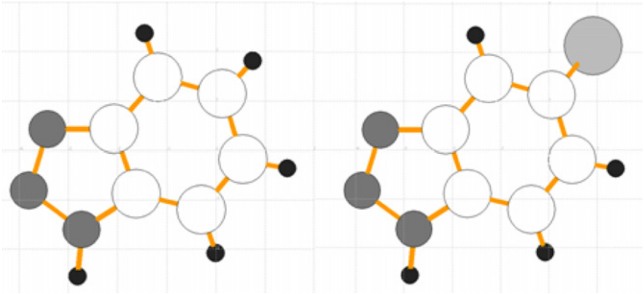

Fig. 1. Structure BTAH and 5-chlor-BTAH.

the thickness of the organic and oxide layers and to extend it to other metals.

2. Experimental

Specimens of metals (mild steel, coppers (99.99%) and zinc (99.98%)) in the form of disks of 10 mm diameter, polished with sandpaper (1000) and diamond powder to mirror finish, degreased with acetone and rinsed by doubly distilled water. A borate buffer solution (pH 7.4) without and with the addition of 5-chloroBTA (Acros Organics) is used in this study. Specimens preliminarily are cathodically activated in a three electrodes cell to remove an air formed oxide in the buffer during 20 min, and then the anodic potential corresponding to the oxide layer formation is applied. Then 5-chloroBTAH is introduced in the concentration optimally corresponding to formation of a monomolecular film, which is defined from ellipsometric data [11]. To remove physically adsorbed molecules of 5-chloroBTAH the specimens are sonicated in bidistillate within 10 min, and then immediately transferred to the spectrometer chamber.

XP spectra of the surface layers formed were registered by means of the special analyzer chamber CLAM100 set on Auger microscope HB100 (Vacuum Generators, GB). Pressure in the analytical chamber was below 10^{-8} Torr. As X-ray source the A1 anode is used (200 W). Analyzer pass energy is set at 50 eV. The spectrometer was calibrated by XPS peaks of metals: Au4f$_{7/2}$ (E_b = 84.0 eV), Cu2p$_{3/2}$ (E_b = 932.5 eV), Fe2p$_{3/2}$ (707.0 eV), Fe3p (53.0 eV), Zn2p$_{3/2}$ (1021.7 eV), and also Auger-spectra CuL$_3$M$_{45}$M$_{45}$ (568.0 eV), ZnL$_3$M$_{45}$M$_{45}$ (494.5 eV), measured after cleaning the surfaces of metals by argon ions. Position of XPS peaks of the corresponding elements is referred to the C1s peak of carbonaceous contamination, whose energy is taken equal to 285.0 eV. For each metal, no less two specimens were analyzed. The peak positions were reproduced better than ±0.15 eV. Deconvolution of spectrums into individual spectra is carried out after the Shirley background subtraction. In the case of Fe2p, Auger-spectra CuLMM and ZnLMM the experimental spectrum is fitted with simulated one by summing the individual spectra for clean metal and oxide taken in necessary proportion. To calculate the thickness of the formed layers for assumed model of the surface film a program MultiQuant developed by Mohai [12] is used, in which the integrated intensity of all elements forming a surface film were taken into account. This software is based on fitting the experimental and calculated integral peak intensities. The formed film was divided in some parallel layers (contamination, inhibitor layer, oxide and metal). It was thus supposed that the corresponding atoms are uniformly distributed in their layers. The cross sections of the electronic shells σ, calculated by Scofield [13] are generally used. For correcting the element sensitivity to account for the specificity of spectrometer, the corresponding peaks of salts with known stoichiometry have been measured and influence of carbonaceous contamination is taken into account. The latter should result in more exact evaluation of layers thickness [14]. The cross sections of the Auger-transitions –CuLMM and ZnLMM, have been determined using peaks Cu2p$_{3/2}$, Cu3p, Zn2p$_{3/2}$, and Zn3p, accordingly from spectra of clean metals. Mean escape depths λ, are calculated according to Cumpson and Seah [15] by program MultiQuant which has also been used for simulating the intensities of the peaks taking into account the thickness of the layers estimated from the experimental values.

3. Results and discussion

3.1. XPS of 5-chloroBTAH

Proton substitution in position 5 by chlorine atom in benzene ring of molecule BTAH, which structure is determined in [16,17], results in a decrease of a dissociation constant from 8.1 to 6.1 that in turn improves interaction of atoms forming azole rings with cations of metals [18–20]. Taking into account the carbonaceous layer, ratio N:Cl in $ClC_6H_3N_3H$ corresponds to formula composition 3:1.

Despite the difference in nitrogen atoms, the N1s spectrum reveals one slightly asymmetric peak at E_b = 401.0 eV (full width at half maximum is 2.9 eV) (Fig. 2a). According to quantum-chemical calculations (method PM3) for the optimized molecule of 5-chloroBTA the charges on nitrogen atoms only slightly differ from each other (HN^1 (+0.18), N^2 (−0.10), N^3 (−0.02)).

Replacement of a labile proton at N^1 with potassium cation narrows the N1s peak (2.4 eV) and shifts it to E_b = 399.4 eV, owing to leveling and increasing of the electronic density on the nitrogen atoms. The binding energies for N1s and Cl2p are fairly within a range for organic compounds [21]. It is worth noting that 5-chloroBTA, adsorbed on a surface of metals, after 2 h X-ray exposure slightly decomposes. Thus both N1s, and Cl2p peaks are displaced toward smaller energies, (∼399 eV and ∼200 eV, accordingly), and intensity of the Cl2p peak decreases. Therefore, studies have been limited by measuring XPS at two angles: at 10° ± 5 (so called "bulk" angle) and 45° ± 5 (so called "surface" angle) relative to normal to a surface. After a run, the sample holder is turned into initial position and a run is repeated for to be sure in reproducibility of spectra.

3.2. XPS of a monomolecular layer 5-chloroBTA on the oxidized surface of mild steel

A few papers are published where the adsorption of BTA on iron and its alloys in particularly in acidic solutions are considered [22–27]. According to our data [28], the adsorption of BTAH on a surface of the oxidized steel results in formation of an overlayer of inhibitor, whose thickness was ∼0.7 nm. The thickness of this layer assumes formation of a monomolecular layer of BTA anions that are almost normal to the surface.

The XPS of an electrode exposed in a buffer solution containing 5-chloroBTA shows the N1s and Cl2p peaks at 400.3 and 201.1 eV, accordingly (Fig. 2a and b). A shift of the N1s peak from 401.0 eV found for the crystalline 5-chloroBTAH to 400.3 eV and the narrowing of the peak width from 2.9 eV to 2.5 eV reveal leveling the electronic density on nitrogen atoms because of deprotonation and formation of the chemical bonding between the nitrogen lone-pair and iron cations. The Fe2p spectrum (Fig. 3a and b) may be fitted with two spectra – the first one is due to metallic state (Fe2p$_{3/2}$ peak at 707.0 eV), the second one specifying the oxidized state (Fe2p$_{3/2}$ peak at 711.4 eV corresponding to Fe_2O_3 covered with FeOOH [29,30]). These spectra well agree with the O1s spectrum, which can be fitted with three components as shown in Fig. 3c.

Assuming a sequential arrangement of parallel layers (carbon contamination, hydroxyl groups and water molecules, 5-chloroBTA, iron oxide) formed on a metallic surface the integrated intensity of peaks of all elements [12] have been used to